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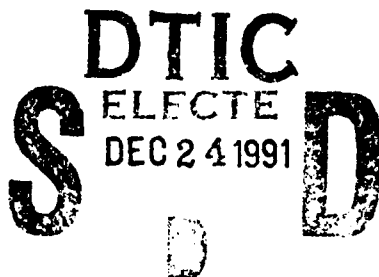
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Organometallic NLO Polymers. Linear Main-Chain NLO Polymers of Ferrocene

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Bis(functionalized) ferrocene NLO-phore monomers were prepared. Several ferrocene NLO-phores were characterized by single-crystal molecular structures. The new ferrocene monomers were successfully polymerized using a Knoevenagel polycondensation technique. The polymers were characterized by spectroscopic and GPC data.					
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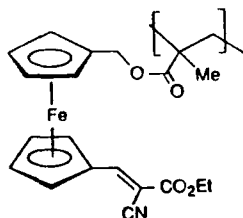
ORGANOMETALLIC NLO POLYMERS. LINEAR MAIN-CHAIN NLO POLYMERS OF FERROCENE

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Introduction

The discovery of ferrocene over four decades ago marked the beginning of organometallic chemistry.¹ The ferrocene unit has proved itself to be a versatile building block with excellent thermal and photochemical stability.² Polymeric materials which contain organometallic moieties have become a well developed and mature subdiscipline of polymer chemistry.³ The ferrocene unit has been incorporated into polymers as a pendant group⁴ and also as part of the polymer backbone.⁵

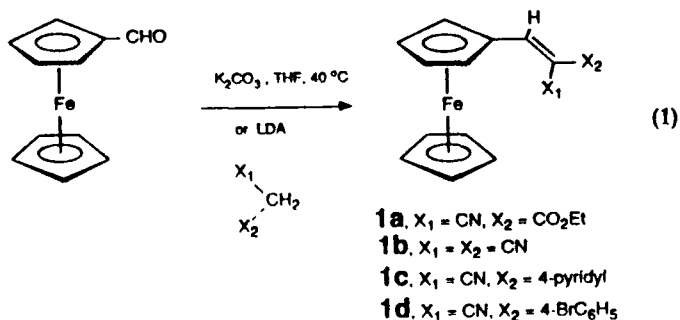


A very recent use of ferrocene complexes has appeared in the area of nonlinear optical (NLO) materials.⁶ Based on both theory⁷ and experimental⁸ data, ferrocene compounds possess large hyperpolarizability values (i.e. β). These data combined with excellent thermal and photochemical stability make ferrocene systems a top organometallic candidate for use in NLO materials.⁹ Our research program has recently demonstrated that a ferrocene complex bound to poly(methyl methacrylate) copolymer can be successfully aligned and exhibit the optical property of second harmonic generation (SHG).¹⁰

We describe herein the synthesis of several novel ferrocene monomers and their utilization in the preparation of main-chain organometallic NLO polymers.

Results & Discussion

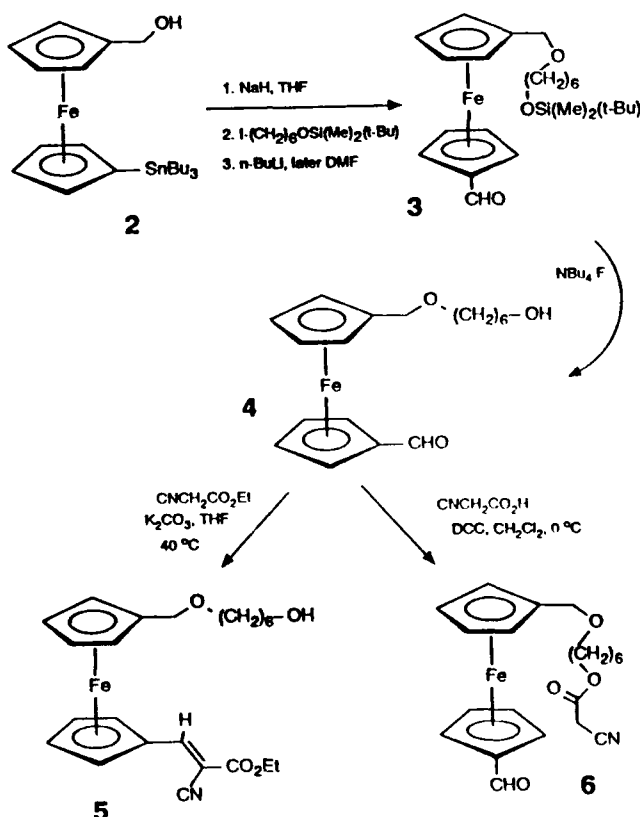
Crystallographic Study of Ferrocene NLO-phores
Treatment of ferrocenecarboxaldehyde with active methylene compounds results in high yields of the condensation product 1 (eq 1).¹¹ For the preparation of 1c and 1d we employed lithium diisopropylamine in place of K_2CO_3 . The reactions proceed in nearly quantitative yield with no apparent side reactions.



Four ferrocene NLO-phores have been characterized by single-crystal molecular structure determinations. Several structural features are worth noting. In all the systems we have prepared to date the cyano group is found in a Z-relationship to the ferrocenyl moiety. The coplanarity of the system appears related to the electronic nature of the substituents on the vinyl group. Notably, the *p*-bromophenyl group in 1d is rotated considerably out plane from the π -system; whereas, it can be seen that the 4-pyridyl in 1c is nearly coplanar with the π -system.

Monomer Synthesis. Through chemistry developed in our laboratory we can prepare complex 2 starting from readily available materials. Compound 2 is smoothly O-alkylated and then treated with *n*-BuLi and DMF to afford complex 3 (Scheme 1). Removal of the dimethyl-*tert*-butylsilyl protecting group using tetrabutylammonium fluoride affords complex 4 which serves as a pivotal intermediate in our synthetic strategy. Treatment of 4 with ethyl cyanoacetate in the presence of potassium carbonate affords monomer 5 in high yield. Coupling of 4 with cyanoacetic acid using dicyclohexylcarbodiimide (DCC) affords the AB monomer 6. Monomer 6 is found to be very base sensitive and rapidly undergoes an intramolecular Knoevenagel condensation which makes purification procedures extremely difficult.

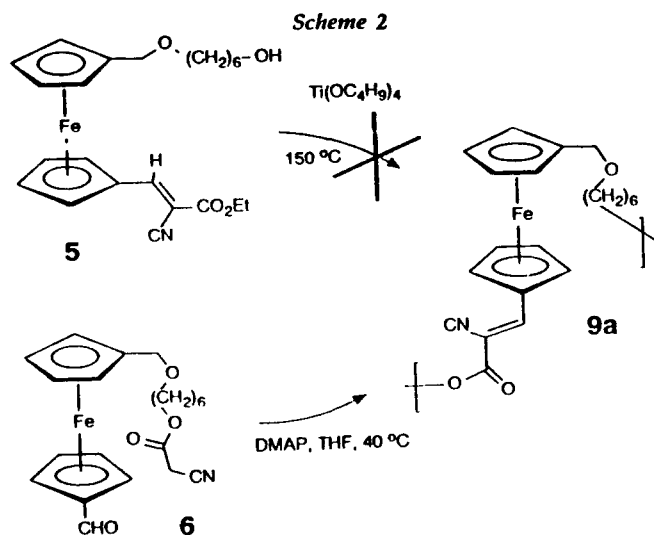
Scheme 1



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Polymer Synthesis & Characterization. We first attempted to polymerize monomer **5** by treatment with $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and heating the mixture to 150°C under a nitrogen atmosphere (Scheme 2). The product of the polymerization reaction was an intractable purple solid. Carrying out the polymerization at 200°C in a neat melt produced a similar intractable purple solid. In this latter reaction we identified 1,6-hexanediol as volatile by-product of the "polymerization" reaction. We seen similar results when polymerizing monomer **7** in that an intractable purple solid was obtained with spectroscopic (IR and UV-Vis) and analytical analogous to that expected for a polyester.



Treatment of **6** with *N,N*-dimethylaminopyridine (DMAP) at 40°C produces polymer **9a**. Polymer **9a** is found to be low in molecular weight ($M_n = \sim 4,500$) with both aldehyde and cyanoacetate end-groups. The polymer is soluble in all organic solvents and displays spectroscopic data consistent with the ferrocenyl NLO-phore (i.e. β -ferrocenyl- α -cyanoacrylate). Further treatment of polymer **9a** ($M_n = \sim 4,500$) with new monomer produced polymer of higher molecular weight ($M_n = 6,700$). We believe a limiting factor in the polymerization of **6** is an intramolecular Koevenagel condensation which competes with polymer formation. The macrocyclic lactone **10a** has been isolated from the polymerization reaction and fully characterized.

Concluding Remarks

Employing the Koevenagel polycondensation reaction affords homopolymers of modest molecular weight. These polymers are tractable materials unlike those obtained through transesterification or neat melt polymerization techniques. Work is continuing on the design of new monomers which are less likely to undergo an intramolecular Koevenagel condensation.

Experimental Section

Polymer 9a A Schlenk flask was charged with THF (3 mL), **6** (0.34 g, 0.83 mmol), and DMAP (0.10 g, 0.83 mmol). The mixture was heated to 40°C and allowed to react for 16 h. The reaction mixture was decanted into pentane (100 mL) and the precipitated polymer collected (0.38 g, 43%). The polymer was contaminated with small amounts of lactone **10a**. GPC analysis of the polymer gave an average molecular weight of $M_n = 4,500$. A THF solution containing the polymer/lactone

mixture (0.03 g) and **6** (0.91 g, 2.21 mmol) was treated with DMAP (0.27 g, 2.21 mmol) to see if the molecular weight could be increased. GPC analysis of this product showed a peak corresponding to an average molecular weight of $M_n = 6,700$. Spectroscopic data for the polymer: ^1H NMR (CDCl_3) δ 8.13 (s, 1 H, CHO), 4.98 (t, $J = 2$ Hz, 2 H, Cp), 4.72 (t, $J = 2$ Hz, 2 H, Cp), 4.29 (t, $J = 2$ Hz, 2 H, ipso-Cp), 4.24 (m, 4 H, Cp and CH_2O), 4.13 (s, 2 H, CpCH_2O), 3.42 (m, 2 H, OCH_2), 1.74 (m, 2 H, CH_2), 1.59 (m, 2 H, CH_2), 1.41 (m, 4 H, CH_2); ^{13}C NMR (CDCl_3) δ 163.2 (CO_2), 158.4 ($\text{CH}=\text{C}$), 116.8 (CN), 86.8 (ipso-Cp), 77.3 (ipso-Cp), 74.6 (Cp CH), 72.2 (Cp CH), 71.2 (Cp CH), 70.8 (Cp CH), 70.4 (CpCH_2O), 68.0 (CH_2O), 66.1 (CH_2O), 29.5, 28.5, 25.7, 25.5 (CH_2 s).

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